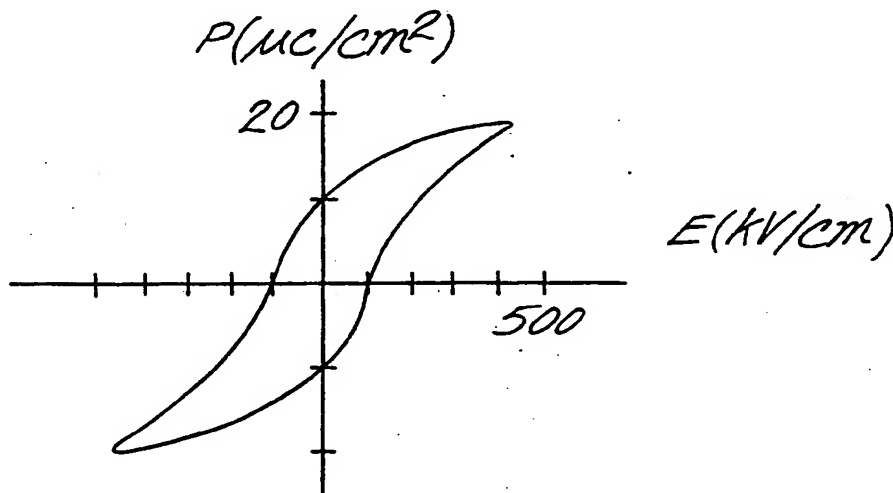


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(54) Title: AMORPHOUS FERROELECTRIC MATERIALS**(57) Abstract**

Amorphous ferroelectric materials are formed by a sol-gel type process and the ferroelectric properties stabilized by complete hydrolysis and polycondensation, and extraction of residual organic materials, preferably by heating at temperatures below the temperature at which crystallization may occur. Stable solutions of metal alkoxides are prepared by reacting or dissolving a metal alkoxide in alcohol such as absolute ethanol. The solution may be spincoated on essentially any substrate, conductor or non-conductor, crystalline or amorphous, transparent or opaque, and even including plastics. Hydrolysis and polycondensation occur in situ to deposit an amorphous ferroelectric film. Residual alcohol is extracted by heating below the temperature at which crystallization occurs. Such films show P-E hysteresis loops and pyroelectric current. Such ferroelectric thin films are useable in electronic, opto-electronic and optical devices.

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AMORPHOUS FERROELECTRIC MATERIALS

Background

This invention relates to ferroelectric materials which are amorphous instead of crystalline. In particular, it concerns a technique for preparing thin films of amorphous ferroelectric material by condensation from a liquid solution containing precursor compounds.

It has been well established that many crystalline mixed oxide compositions such as barium titanate, BaTiO_3 , LiNbO_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$, $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$, and the like, are ferroelectric in nature and both single crystal and polycrystalline forms of these materials have large numbers of practical and potential applications in electronic, opto-electronic, nonlinear optical and piezo-electric devices. Such applications include, for example, optical wave guides, electro-acoustic transducers, high frequency surface acoustic wave devices, pyroelectric infrared detectors, ferroelectric memory cells, ferroelectric photoconductor displays, optical modulators, field effect transistors, metal/insulator/semiconductor transistors and the like.

For many years, it has been believed by the scientific community that ferroelectricity can only exist in a crystalline material with long range order. In 1977, a theoretical discussion suggested that the presence of ferroelectricity in an amorphous glass was

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1 not excluded on theoretical grounds and a model for a
possible amorphous ferroelectric material was proposed.
"Microscopic model for a ferroelectric glass" by M.E.
Lines, Physical Review B, 15 (January 1, 1977).

5 Since then, there have been sporadic efforts to
produce an amorphous ferroelectric material without
apparent success. Techniques for producing amorphous
materials have included RF sputtering or in at least
10 one case by extremely rapid quench freezing of molten
lithium niobate and lithium tantalate. "Anomalous
dielectric behavior and reversible pyroelectricity in
roller-quenched LiNbO_3 and LiTaO_3 glass", by A.M. Glass,
M.E. Lines, K. Nassau and J.W. Shiever, Applied Physics
15 Letters, 31 (August 15, 1977). Tantalizing hints of
ferroelectricity such as anomalies in the dielectric
constant have been noted in amorphous materials. In
addition, Glass, et al. noted a pyroelectric response.
However, they concluded that "these observations are
consistent with ferroelectric behavior, but not
20 conclusive . . . "

To unambiguously show ferroelectricity in a
material, it is generally regarded that the most
significant indication of ferroelectricity is the well
known P-E hysteresis loop. The polarization P as a
25 function of the electric field E shows a characteristic
hysteresis loop in an alternating field due to the
field required to reverse polarization. Another
important criterion is the presence of pyroelectric
current, namely current flow from a poled material as
30 temperature is changed.

Ferroelectric materials also have a ferroelectric
to paraelectric phase transition temperature T_c ,
sometimes referred to as the Curie temperature. A
material may be ferroelectric below the Curie
35 temperature and it loses ferroelectricity abruptly at
this temperature. One may also observe ferroelectric
domains in the material and a dielectric anomaly is

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1 likely to be observed. This anomaly may take the form
of three or four orders of magnitude increase in
dielectric constant near the Curie temperature.

5 Some of these phenomena may not be observed in a
given sample. More than one of these phenomena should
be observed to unambiguously determine that there is
ferroelectricity. Observation of a P-E hysteresis loop
is regarded as proof of ferroelectricity, although it
is still desirable to confirm this by observing pyro-
10 electric current and other ferroelectric phenomenon.

Existing metal oxide-based ferroelectrics fall
into two general categories, single crystals and
polycrystalline ceramics. Single crystals are
typically grown from melts at high temperatures by
15 slowly cooling down certain regions of the melt and
allowing the growth of a single crystal. A Czochralski
technique may be used. Polycrystalline ceramics may be
made through solid state reactions of powders or from
a melt. Thin films of ferroelectric material may be
20 made in the form of single crystals or in a poly-
crystalline form. These thin films have principally
been obtained by vapor-phase deposition and sputtering,
followed by heating to fully crystallize the deposited
film.

25 It has now been discovered that stable
ferroelectricity can be produced in amorphous materials
formed by a modified sol-gel technique. The
ferroelectric effect has not only been found in mixed
metal oxides known to be ferroelectric in their
30 crystalline state, but also in certain single metal
oxides never previously known to be ferroelectric. The
materials are stabilized, for example, by heating, so
that stable ferroelectric properties persist during use
of the films.

35 In recent years, the so called sol-gel technique
has been used for preparing crystalline metal
oxide-based ferroelectric materials in either thin film

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1 or powder form. This technique employs organometallic
compounds or metal alkoxides to make a homogenous
solution. The solution is typically hydrolyzed to
5 produce a gel which may be precipitated, dried and
crushed to form a powder, or the solution may be used
for coating a thin film on a substrate. The powders or
thin films are then heated above a crystallization
temperature to produce a polycrystalline ferroelectric
material.

10 Research has been directed to the deposition and
crystallization parameters of the technique on the
premise that to obtain ferroelectricity full
crystallization is necessary. The morphology of the
polycrystalline film has been a major concern since it
15 in large part dictates the characteristics of the film.
Since there are shortcomings due to grain boundaries in
polycrystalline thin films, efforts have also been
directed toward growing single crystal films by the
sol-gel technique.

20 It is desirable to have a technique for forming a
ferroelectric material which can be processed at low
temperatures so that there is greater freedom in
selection of materials compatible with processing of
the ferroelectric material. It is desirable that the
25 technique for producing the ferroelectric material be
suitable for forming thin films for use in modern
electronic and optical devices.

Brief Summary of the Invention

30 Thus, in practice of this invention according to
a presently preferred embodiment, an amorphous
ferroelectric material is made by preparing a liquid
solution containing at least one precursor compound for
the ferroelectric material. Solvent is removed to
35 leave an amorphous ferroelectric solid. This solid
ferroelectric material is then stabilized at
temperatures less than sufficient to crystalize the

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1 amorphous material for minimizing changes in
ferroelectric properties. During solvent removal,
hydrolysis and polycondensation may occur.

Amorphous ferroelectric materials include
5 compositions which, when crystallized, have the crystal
structure of known ferroelectric crystals, such as
 BaTiO_3 , $(\text{Sr}, \text{Ba})\text{Nb}_2\text{O}_6$, LiNbO_3 , $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ and
 $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$. The ferroelectric materials include
nonstoichiometric mixed metal oxides such as
10 $2[\text{Li}_x\text{Nb}_{(1-x)}\text{O}_y]$ where x is in the range of from 0 to 0.5
and $y = (5-4x)/2$ and $\text{Pb}(\text{Zr}_x\text{Ti}_{(1-x)})\text{O}_3$ where x is in the
range of from 0 to 1. The first example includes a
single metal oxide Nb_2O_5 . Other single oxides in
amorphous form which show P-E hysteresis include ZrO_2 ,
15 SnO_2 , TiO_2 , Y_2O_3 , BaO , SiO_2 and B_2O_3 , for example. The
ferroelectric effect is independent of the substrate on
which a thin film is deposited and the substrate may
include organic polymers such as electrically
conductive polymers. Electronic, optoelectronic and
20 optical devices may employ amorphous ferroelectric
films.

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1 Brief Description of the Drawings

5 These and other features and advantages of the present invention will be appreciated as the same becomes better understood by reference to the following detailed description when considered in connection with the accompanying drawings wherein:

FIG. 1 illustrates an exemplary P-E hysteresis loop of an amorphous ferroelectric material;

10 FIG. 2 illustrates pyroelectric current of an amorphous ferroelectric film;

FIG. 3 illustrates an exemplary electronic device employing an amorphous ferroelectric film;

FIG. 4 illustrates an exemplary optoelectronic device employing a ferroelectric film; and

15 FIG. 5 illustrates an exemplary optical device employing an amorphous ferroelectric thin film.

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1 Detailed Description

 Very generally speaking, a sol-gel process for forming an amorphous ferroelectric material starts with formation of a solution containing one or more
5 organo-metallic compounds forming a precursor for the thin film. For example, for a binary metal oxide ferroelectric, the solution may contain appropriate proportions of two metal alkoxides which may react to form a double metal alkoxide, or which may remain
10 separately in solution. In some cases, water may be added to the solution to cause formation of a gel.

 Such a solution or gel may be applied to a substrate to form a thin film or the gel may be dried in bulk. The dried solid may be pulverized to form a
15 ferroelectric powder. Alternatively, the metal alkoxide solution may be applied to a substrate to form a thin film and hydrolyzed in situ to form an amorphous ferroelectric thin film.

 The amorphous ferroelectric material is
20 stabilized, typically by heating to a relatively low temperature in a suitable atmosphere for complete hydrolysis and removal of organic materials.

 An example of the formation of a ferroelectric thin film involves stoichiometric lithium niobate,
25 LiNbO_3 , which is known to be a ferroelectric in its crystalline state. Lithium metal is reacted with absolute ethyl alcohol, forming a solution of LiOC_2H_5 . A typical concentration of the lithium ethoxide is in the range of from 0.2 to 0.6 Mol/l. To this solution,
30 there is added an equal amount of $\text{Nb}(\text{OC}_2\text{H}_5)_5$ in the form of a commercially available 99.99% pure liquid. The niobium ethoxide may be simply poured into the lithium ethoxide solution since precipitation is not a problem. The solution is then boiled and refluxed for 24 hours
35 with a water cooled reflux condenser.

 Lithium and niobium ethoxides are known to form an intermolecular complex sometimes referred to as a

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1 double alkoxide upon extensive refluxing. This double
alkoxide, which is soluble in ethyl alcohol, in its
crystalline form closely resembles the local atomic
5 configuration of crystalline LiNbO_3 . In the ethyl
alcohol solution, the $\text{LiNb}(\text{OC}_2\text{H}_5)_6$ double alkoxide is
stable and may be detected by FTIR and NMR. Hydrolysis
and polycondensation of the double alkoxide produces a
lithium niobate having the composition of the alkoxide
precursors.

10 The entire synthesis, mixing and reflux is
conducted in a dry nitrogen glove box. Reflux may also
be conducted outside a glove box with a thorough
desiccant connected to the outlet of the condenser. It
is important for maintaining shelf life to avoid
15 introduction of water. Preferably air is excluded to
exclude water vapor. A small amount of water may
reduce the shelf life of the solution to a few days or
even hours whereas a solution substantially free of
water and isolated from the air as an essentially
20 unlimited shelf life.

A solution prepared in this manner may then be
used for coating a thin film on a selected substrate by
conventional spin casting. In this technique, a
substrate is secured to a spinner, typically with a
25 vacuum chuck. The substrate is rotated at a selected
speed to spread a liquid in a thin film. The thickness
of the film obtained depends on a number of parameters
including rotation speed (higher speed produces a
thinner film), solute concentra-tion (increased
30 concentration of the organometallic produces an
increased thickness), relative humidity (higher
humidity produces a thicker film), and temperature
(generally speaking, higher temperature produces a
somewhat thinner film).

35 It is desirable when casting and hydrolyzing the
thin films of amorphous ferroelectric material to have
a low relative humidity. Preferably, the relative

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1 humidity in the air during casting and initial
hydrolysis is in the range of from 10 to 25%. Some
humidity is desirable to assure hydrolysis and
polycondensation of the ferroelectric material. High
5 relative humidity may induce such rapid hydrolysis that
the homogeneity of the film is jeopardized. Very high
relative humidity may also produce a thick film that is
subject to cracking. A relative humidity as high as
50% may be tolerated for some films. Hydrolysis in
10 such a high relative humidity may be largely complete
in a minute or so. The hydrolysis reaction occurs
rapidly, but evaporation of the resultant alcohol may
be impeded.

Film thicknesses from 500 to 6000 Angstroms may be
15 formed. If desired, a thicker film may be obtained by
permitting the film to stand in air for a sufficient
period to largely complete hydrolysis at least at the
surface. The hydrolyzed solid is essentially insoluble
in the solution. Substantially complete hydrolysis can
20 be obtained in no more than a few minutes, then another
drop of solution may be added to the substrate on the
spincaster. If one tries to produce too thick a film
with this technique, there may be cracking.

If desired, one may make a thicker film in several
25 layers with stabilization of the underlying films.
With intermediate stabilization of the film by heating,
cracking may be minimized.

When the metal alkoxide is contacted by water,
such as the water vapor present in air, there is
30 polycondensa-tion of a polymer having
metal-oxygen-metal bonds. The alkyl group is released
as the corresponding alcohol. Typically the solvent
used is the same as the alcohol released.

When water is added to the solution before forming
35 a thin film, a prepolymer may be formed as particles in
a gel. The gel may be completely hydrolyzed and
solvent extracted to form a more or less solid body.

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1 Such a body may be crushed to form a ferroelectric
powder. The prepolymer may be coated on a substrate by
spraying, dipping, spincasting, or the like, with
hydrolysis and complete polymerization occurring in
5 situ on the substrate.

When dipping film thickness is controlled by speed
of withdrawal of the substrate from the solution,
temperature, solute concentration, and relative
humidity. Ordinary, normal room temperature and
10 humidity conditions fall within the desired temperature
and humidity range for dip coating.

Prepolymerization by adding water to the solution
may reduce the shelf life of the solution. It may also
lower the crystallization temperature of the amorphous
15 material. Thus, it is preferred to deposit films from
solutions free of water, or at best, with water added
only a short time before deposition.

After spincasting, the film is stabilized for
minimizing future changes in ferroelectric properties.
20 The as-cast film includes organic materials which may
comprise some of the alkoxy compound which is not yet
hydrolyzed, the released alcohol from the hydrolysis,
and the alcohol solvent. Heating of the amorphous
ferroelectric material at a temperature less than
25 sufficient to cause crystallization can quickly
stabilize the film. The heating accelerates hydrolysis
and vaporization of the solvent. Heating in air at
100°C for as little as two hours can reduce the organic
content of the film from about six mol percent to one
30 mol percent. Higher temperatures may be used for
stabilization without crystallizing the film. Heating
may be in air or an inert atmosphere. Water vapor may
be present in the atmosphere during heating to assure
complete hydrolysis.

35 In one example, a thin film of lithium niobate
amorphous ferroelectric material had a thickness of
about 1100 Angstroms. It was stabilized by heating in

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1 air for one hour at 200°C. The composition profile of
the film was measured by Auger analysis. The nominal
composition of the film after stabilizing was
5 $\text{Li}_{1.01}\text{Nb}_{0.99}(\text{OC}_2\text{H}_5)_{0.006}\text{O}_{2.75}$. Thus, the organic content of
the film was about one percent. The reason for the
apparent deficiency of oxygen is not clear.

It is desirable that the amorphous material be
essentially completely hydrolyzed before appreciable
heating. This is significant to help avoid oxidation
10 of the organic material with the possible consequence
of producing a metal carbonate which is not ferro-
electric. Generally speaking, oxidation is undesirable
since it tends to reduce the remanent polarization of
the ferroelectric material. If desired, oxidation may
15 be largely eliminated by casting and hydrolyzing a thin
film of amorphous ferroelectric material in a moist
nitrogen environment.

The ferroelectric properties of a film are
apparently unaffected by the substrate on which the
20 film is deposited. Indicative of that is confirmation
of ferroelectric properties of films deposited on
amorphous silicon carbide, semiconductors such as
silicon (n-type, p-type or intrinsic) and gallium
arsenide, insulators such as fused quartz, Pyrex
25 borosilicate glass, aluminum oxide, and magnesium
oxide, metals such as gold, platinum, aluminum, and
iron, conductors such as indium tin oxide, polypyrrole,
and polyaniline, and ferroelectric materials such as
lithium tantalate and single crystal lithium niobate.
30 This shows the versatility of amorphous ferroelectric
materials for a broad variety of applications.

The ferroelectric material is stabilized by
heating in air to a sufficient temperature to complete
the hydrolysis and drive off remaining organic
35 material. The temperature required depends on the
thickness of the film, relative humidity, the solvent
employed, reaction products from the precursors,

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1 temperature resistance of the substrate and the
crystallization temperature of the amorphous ferro-
electric material.

5 The as deposited film contains alkoxy and hydroxy
groups, for example. These continue to undergo
reaction and evaporation after deposition. Although
the as deposited films show ferroelectric behavior, the
characteristics are not stabilized until these groups
are removed or otherwise stabilized.

10 For example, thin film lithium niobate
crystallization commences in the range of from 350 to
450°C depending on conditions. Stabilization of the
amorphous material is therefore desirably conducted at
a temperature of up to about 250°C to assure that there
15 is no crystallization. The time of heating depends on
temperature, with higher temperatures requiring shorter
heating cycles. Preferably, the heating rate is in the
range of from about 1° to 5°C per minute. A relatively
low heating rate is desirable to avoid cracking, with
20 slower rates being preferred for thicker films. Time
is required for solvent to diffuse from the film and
for structural relaxation to occur. It is noted that
during stabilization, shrinkage of as much as 50% of
film thickness may occur.

25 Stabilization may also be obtained by assuring
that there is ample exposure to water vapor at room
temperature, and the film may be further consolidated
by enhancing the evaporation of solvent in a vacuum
system.

30 Heating in air to a temperature in excess of the
expected service temperature of the product employing
the ferroelectric material remains the preferred
technique for stabilizing the film. Stabilizing a film
at somewhat elevated temperatures is desirable for
35 producing a relatively dense film. A denser film
provides a higher remanent polarization P_r . In the
tests to date, values of P_r of from 6 to 18 have been

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1 observed, which is within the range of ferroelectric
thin films currently in use.

5 The low temperatures needed for stabilizing are
particularly attractive for formation of a ferro-
electric thin film on a plastic substrate. For
example, it has been shown that an amorphous ferro-
electric thin film can be formed on electrically
conductive polymers such as polypyrrole and
polyaniline. This provides the ability to form a
10 somewhat flexible ferroelectric device.

Ferroelectricity may be caused by several entirely
different mechanisms. A common feature for all known
ferroelectric materials is the existence of electric
dipoles prior to the application of an external
15 electric field, wherein the dipole direction can be
effectively reversed by application of an electric
field. Probably the most commonly mentioned example is
a barium titanate crystal, BaTiO_3 , consisting of oxygen
octahedra with a Ti^{4+} cation enclosed near the center of
20 the oxygen octahedron. Because of the size of the
ions, there is enough room in such an octahedron for
the Ti^{4+} ion to "rattle" between corners of the
octahedron. At room temperature, this "rattling cage"
remains stationary with the cation off-center near one
25 of the corners of the octahedron. This asymmetry
creates an electric dipole.

Under the influence of an external electric field,
the relative positions of the Ti^{4+} and O^{2-} ions can be
changed so that the center of their corresponding
30 charges shift from the equilibrium positions in the
octahedron in opposite directions along the electric
field. When the electric field direction reverses, the
original dipole direction can in turn be reversed by
overcoming a potential barrier. In the case of barium
35 titanate, it is commonly recognized that the potential
barrier is caused by the combination of spontaneous
polarization of the dipoles on a macroscopic scale

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1 (usually referred to as the formation of domains) and
an inherent potential barrier at a microscopic scale.
It is the reversibility of the dipoles and the
5 existence of the potential barrier that results in the
well-known P-E hysteresis behavior which is
characteristic of ferroelectric materials.

In practice of this invention, the importance of
the octahedron structure is recognized. When making an
amorphous ferroelectric material, one seeks to recreate
10 the nearest neighbor structure of the corresponding
crystalline ferroelectric material and at the same time
maintain a long range disorder. With this in mind, one
may, through polycondensation of an organometallic
compound, produce amorphous ferroelectric films of
15 virtually every known metal oxide-based ferroelectric
material.

However, it appears that close resemblance of the
local structure to corresponding crystalline ferro-
electric materials does not appear to be necessary. A
20 necessary and sufficient condition for ferroelectricity
is the existence of a reversible electric dipole and
potential barrier that resists the reversal or
annihilation of the dipole. Thus, there are a number
of amorphous metal oxide systems in both mixed oxides
25 and amorphous single metal oxides which are ferro-
electric where it is not certain that an octahedral
local structure is present.

Amorphous ferroelectricity has been observed in a
broad variety of materials. This has been shown by the
30 P-E hysteresis curves. FIG. 1 illustrates an exemplary
P-E hysteresis curve at 50 Hz for a lithium niobate
sample deposited on a gold coating on a silicon wafer.
The film was stabilized at 250°C for one hour. This is
neither the best nor worst hysteresis curve observed,
35 but is merely exemplary.

A modified Sawyer-Tower bridge was used for the
P-E hysteresis measurements. Most hysteresis curves

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1 were observed at 50 Hz. Some observations were made at
frequencies as high as 12 kHz for verifying that the
hysteresis loops seen were not due to space charge or
5 other possible low frequency effects in the dielectric
material.

In a typical hysteresis test set up, the substrate
is electrically conductive. A metal "spot" of known
area is sputtered on the surface of the thin film.
Electrical contact is made to the metal spot and the
10 conductive substrate for connection in the bridge.

In order to exclude any possible interface effects
between a gel film and the substrate, a ground powder
of bulk gel was used to independently confirm the
hysteresis loops. For example, a lithium-niobium
15 ethoxide solution was hydrolyzed and dried. The
resultant solid amorphous lithium niobate was
pulverized to form a powder and was stabilized at 100°C
for two hours in air. The gel powder was dispersed in
acetone and dropped on the polished surface of a copper
20 plate. A second copper plate was then pressed onto the
other side of the powder layer to form a sandwich with
the copper plates forming the electrical contacts for
the bridge. The same type of hysteresis loops were
obtained for the powder as for a thin film of similar
25 material.

Another independent verification of amorphous
ferroelectricity estimated the characteristic Maxwell
relaxation time of a thin film deposited on fused
quartz and stabilized at 100°C. A relaxation time in
30 the order of 10^4 seconds was estimated, corresponding to
 10^{-4} Hz, too slow to contribute to the hysteresis loop
measurements which were at 50 Hz and higher. The
electrical conductivity was measured at about $10^{-6}/\Omega\text{-cm}$.

Another verification of ferroelectricity is
35 illustrated in FIG. 2. A sample of amorphous
ferroelectric lithium niobate was poled by cooling from
75°C in a d.c. electric field. After space charges

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1 were eliminated, pyroelectric coefficient was measured
during reheating several hours after poling. FIG. 2
illustrates dP/dT as a function of temperature where P
is the peak saturation polarization and the units of
5 the pyroelectric coefficient are nanocoulombs per cm^2K .

That the ferroelectric material was amorphous was
confirmed by X-ray diffraction and electron
diffraction. An electron diffraction pattern shows
only diffuse rings. The observable limit of
10 crystallite size in the X-ray diffraction is
approximately 100 angstroms, while that of electron
diffraction was 20 Angstroms. No crystallites were
observed. Both of these tests indicate the basically
amorphous nature of the film. If there were any small
15 crystallites, they were necessarily smaller than 20
angstroms.

Another significant amorphous ferroelectric
material comprises barium titanate. The solution for
depositing a film of barium titanate is made by first
20 dissolving titanium isopropoxide in isopropyl alcohol.
Next, one gradually adds barium n-butoxide gradually
while stirring vigorously so that no precipitation
occurs. The proportions of barium and titanium in the
solution are equal so that a stoichiometric double
25 alkoxide is formed and the solution and barium titanate
is condensed. The total concentration is in the range
of from 0.2 to 0.6 Mol/l. The solution is refluxed for
several hours. It is important to form this solution
in the absence of moisture since the composition
30 hydrolyzes quite readily. A double alkoxide forms
rapidly with only an hour of reflux. A thin film
deposited from the solution forms a ferroelectric
amorphous film of barium titanate.

A particularly useful amorphous ferroelectric
35 material is known as PZT, which has the formula
 $\text{Pb}(\text{Zr}_x\text{Ti}_{(1-x)})\text{O}_3$, where x is in the range of from 0 to 1.
A specific example shown to be ferroelectric comprises

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1 $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$. Precursors for PZT include titanium
isopropoxide and zirconium n-propoxide. The zirconium
and titanium alkoxide compounds are mixed in
isopropanol. Separately, one dissolves lead acetate in
5 isopropanol. The lead isopropanol solution is very
gradually added to the zirconium-titanium solution with
vigorous stirring. The solution is refluxed for one to
eight hours. The solution does not form a double
alkoxide like the lithium-niobium system, but is a true
10 solution of the three precursor compounds. Refluxing
is to assure homogeneity rather than to promote
reaction.

Another useful amorphous ferroelectric material,
sometimes referred to in its crystalline form as SBN is
15 strontium barium niobate having the formula
 $(\text{Sr}_x\text{Ba}_{(1-x)})\text{Nb}_2\text{O}_6$ where x is in the range of from 0.25 to
0.75. An exemplary composition shown to be ferro-
electric comprises $(\text{Sr}_{0.6}\text{Ba}_{0.4})\text{Nb}_2\text{O}_6$. The solution for
depositing SBN is made by reacting strontium metal with
20 absolute ethanol to form a first solution of strontium
ethoxide. A separate solution of barium ethoxide is
formed by reacting barium metal with absolute ethanol.
Appropriate proportions of the solutions are then mixed
together. An appropriate amount of liquid niobium
25 ethoxide is slowly dropped into the mixed solution with
vigorous stirring. The resultant solution is refluxed
for about five hours. Typical concentration of the
solutes in the solvent is in the range of from 0.2 to
0.6 Mol/l. The SBN precursor composition is extremely
30 sensitive to moisture and the reactions are conducted
and the product stored in a dry nitrogen environment.
A thin film of amorphous SBN may then be formed by
spincasting or by spraying or dipping.

Other amorphous oxide-based ferroelectric
35 materials may be made by a similar technique of forming
or dissolving metal alkoxides or other organometallic
compounds in an organic solvent, and hydrolyzing the

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1 solute in the resulting solution either in bulk, or during or after deposition as a thin film.

Another useful amorphous ferroelectric material comprises PLZT, a mixed metal oxide of lead, lanthanum, zirconium and titanium. Other ferroelectric materials include $\text{Pb}_{0.92}\text{Bi}_{0.07}\text{La}_{0.01}(\text{Fe}_{0.405}\text{Nb}_{0.325}\text{Zr}_{0.27})\text{O}_3$, LiTaO_3 , $\text{Bi}_4\text{Ti}_3\text{O}_{12}$, potassium niobate, lead zirconate-lead titanate nonstoichiometric solid solutions, lead titanate, lead niobate, lead tantalate, lead bismuth niobate, lithium tantalate, sodium vanadate, silver vanadate, barium lithium oxyfluoroaluminate, $\text{Ba}(\text{Al}_{1.4}\text{Li}_{0.6})(\text{O}_{2.8}\text{F}_{1.2})$, and lead iron niobate, $\text{Pb}_2(\text{Fe},\text{Nb})\text{O}_6$. Other ferroelectric materials may be produced which have Curie temperatures substantially below room temperature such as potassium tantalate, sodium niobate, cadmium titanate, strontium (pyro)tantalate, tungsten trioxide and the like.

It should be noted from the disclosures above that an amorphous ferroelectric material of mixed metal oxides may be produced with a nonstoichiometric composition. Thus, amorphous ferroelectric materials include $2[\text{Li}_x\text{Nb}_{(1-x)}\text{O}_y]$ where x is in the range of from 0 to 0.5 and y is $(5-4x)/2$, $\text{Pb}(\text{Zr}_x\text{Ti}_{(1-x)})\text{O}_3$ where x is in the range of from at least 0 to 1 and $(\text{Sr}_x\text{Ba}_{(1-x)})\text{Nb}_2\text{O}_6$ where x is in the range of from 0.25 to 0.75.

The following table shows the compositions and properties of stoichiometric lithium niobate, nonstoichiometric LN compositions and niobium oxide which surprisingly in the amorphous form is ferroelectric.

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TABLE 1

Composition	LiNbO ₃	Li _{0.33} Nb _{1.67} O _{4.34}	Li _{0.25} Nb _{1.75} O _{4.5}	Nb ₂ O ₅
Film Thickness (Å)	2100 2870	2300	2560	
P _r (μC/cm ²)	10 18	14	9	
E _c (kV/cm)	110	86	65	
Refractive Index	24 1.43 1.15	1.13	1.13	
Pyroelectric Coefficient @ 28°C (nC/cm ² K)	24 8 5	---	---	
Dielectric Constant	---	---	---	

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1 All of the samples listed in the table were
deposited as a thin film on a gold substrate (a film of
gold on a silicon substrate) for P-E hysteresis
5 measurements. The samples were stabilized at 100°C for
two hours in air. The magnitude of the remanent
polarization P_r is in the order of 20% of the
polarization of single crystal LiNbO_3 .

The pyroelectric current was measured for the two
samples indicated with films deposited on n-type
10 silicon (111) single crystal wafers. The amorphous
films were spin-coated on the polished surface of the
silicon wafer and stabilized at 100°C for five hours in
air. Gold was sputtered onto the surface of the film
to form the top electrode with the silicon used as the
15 other electrode.

The sample was then preheated to 75°C and a DC
voltage of five volts was applied across the electrode
and maintained as the sample was slowly cooled down to
room temperature. The five volt bias was removed at
20 room temperature and the electrodes electrically
connected through a picoammeter for measuring current
while the sample was reheated at a constant heating
rate up to 75°C. This allowed measurement of the
depolarization current as a function of temperature.
25 After again cooling to room temperature, a third cycle
of heating to 75°C was conducted and the pyroelectric
current was monitored.

The junction current which is a function of
temperature was measured first. After poling the film
30 by cooling with an applied DC voltage, the current was
measured during the second heating. This current is a
sum of the junction current, a depolarization current
and the pyroelectric current. The pyroelectric current
is measured on the third heating and from that the
35 pyroelectric coefficient as a function of temperature
can be calculated.

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1 A particularly surprising discovery is that an
amorphous film of niobium oxide, Nb_2O_5 , deposited from
solution is ferroelectric. Further investigation has
established that amorphous zirconium oxide, tin oxide,
5 titanium oxide, yttrium oxide, barium oxide, silicon
oxide and boron oxide are also ferroelectric and may
be stabilized as amorphous ferroelectric materials
(e.g. by heating at 260°C for one hour in air). Such
materials are not known to be ferroelectric in their
10 crystalline form. This is probably due to the symmetry
in their crystalline form which prevents a dipole
moment. On the other hand, the amorphous material has
distortion that breaks down the symmetry and may be
ferroelectric.

15 It is believed that other single metal oxides in
amorphous form as described herein are also ferro-
electric including, for example, oxides of vanadium,
hafnium, tungsten, lanthanum and the lanthanide metals.

 As an example of an amorphous ferroelectric single
20 metal oxide, one can refer again to niobium oxide,
 Nb_2O_5 . A solution for producing amorphous niobium oxide
has niobium ethoxide dissolved in absolute ethanol. A
thin film of niobium oxide was deposited on n-type
silicon (111) and the properties measured. A film
25 having a thickness of 1600 angstroms was spincast and
retained at room temperature in air for five hours for
hydrolysis and polycondensation. The remanent
polarization P_r was $9.7 \mu\text{C}/\text{cm}^2$ and coercive field E_c was
measured at $3.7 \text{ kV}/\text{mm}$. The pyroelectric coefficient
30 was $8.1 \text{ nC}/\text{cm}^2\text{K}$. X-ray diffraction showed that the film
was amorphous.

 Another film of the same material was heated for
five hours at 350°C in air. The film thickness was
1250 angstroms, P_r was 12.2 and E_c was 5.4. X-ray
35 diffraction showed that this film was also amorphous.

 A similar film was heated for five hours at 450°C
in air. The film thickness was 1250 angstroms. P_r was

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1 7.95 and E_c was 6.0. The pyroelectric coefficient was
88. X-ray diffraction showed peaks coincident with
those of gamma-phase Nb_2O_5 .

5 Thus, it was shown that gamma niobium oxide has
P-E hysteresis behavior indicating its ferro-
electricity. P-E hysteresis was also measured using
the copper/oxide powder/copper sandwich mentioned above
for alpha-phase niobium oxide, gamma-phase niobium
oxide, and rutile, TiO_2 .

10 Thus, ferroelectric behavior has been observed for
certain crystalline single metal oxides not previously
identified as ferroelectric.

15 Amorphous ferroelectric thin films are useful in
a broad variety of electronic, opto-electronic and
optical devices where polycrystalline ferroelectric
materials may also find utility. Thus, for example,
FIG. 3 illustrates an exemplary field effect transistor
employing an amorphous ferroelectric thin film. Such
a transistor is formed on an n-type silicon substrate
20 10. P-type dopants are diffused into the substrate to
form a source 11 and drain 12. A thin film of
amorphous ferroelectric material 13 such as lithium
niobate is deposited on the silicon surface between the
source and drain. Metal films are deposited to form a
25 source electrode 14 and drain electrode 15 connected to
the source and drain, respectively. A metal film gate
electrode 16 is deposited on a portion of the gate 13
for control of the transistor. Such an
metal\ferroelectric\semiconductor transistor may be a
30 discrete component or a component in an integrated
circuit.

35 FIG. 4 illustrates schematically an opto-
electronic, ferroelectric-photoconductor memory device.
Such a memory device has a substrate electrode 17 on
which is deposited a ferroelectric thin film 18 such as
lithium niobate. The amorphous ferroelectric film is
surmounted by a conventional deposited photoconductor

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1 film 19 and transparent electrode 20. The two
electrodes are connected to a drive voltage source 21.
A data signal may be read out across a capacitor 22
connected across the electrodes of the memory device.
5 Data are written into or read out of the ferroelectric
layer from the memory chip when both voltage pulses are
applied and light is pulsed onto the photoconductor
film through the transparent electrode. Such an opto-
electric device may be incorporated in an integrated
10 circuit with a variety of other opto-electronic and
electronic components.

In any of the electronic or opto-electronic
devices, it may be highly advantageous to pole the
ferroelectric material by applying an electric field
15 and cooling the material from a temperature above the
expected surface temperature of the device as described
above.

FIG. 5 illustrates a fragment of an exemplary
optical device employing an amorphous ferroelectric
20 material. In a simple example, such an optical device
comprises a ferroelectric crystal 23 such as barium
titanate. An amorphous ferroelectric thin film 24 of
barium titanate is deposited on a surface of the ferro-
electric crystal. Since the film is amorphous, it has
25 a slightly different index of refraction from the
crystal even when chemically similar so that it can
serve as a ferroelectric window. It may be
particularly advantageous in such an optical device to
employ a nonstoichiometric amorphous thin film for
30 obtaining a desired index of refraction.

Various of the amorphous ferroelectric materials
may be doped with small amounts of other elements for
tailoring the ferroelectric, dielectric and optical
properties for a selected application. It should also
35 be recognized that the ferroelectric properties such as
P-E hysteresis and dielectric properties of the thin
film may be selected by varying the nonstoichiometric

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1 composition or by depositing multiple layers of
amorphous ferroelectric materials of different
composition.

5 Although a considerable variety of amorphous mixed
metal oxides and single metal oxides have been shown to
be ferroelectric, it will be understood that additional
similar oxides of stoichiometric and nonstoichiometric
compositions may have equivalent ferroelectricity.
10 Examples have been given of techniques for forming
amorphous ferroelectric materials by a modified sol-
gel process. Many additional modifications of the
process for producing amorphous ferroelectric materials
will be apparent to those familiar with such processes.
15 It is therefore to be understood that within the scope
of the appended claims, this invention may be practiced
otherwise than as specifically described herein.

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1 **WHAT IS CLAIMED IS:**

1. An amorphous ferroelectric material prepared by the steps of:

5 preparing a liquid solution containing at least one precursor compound for the material;

 removing the solvent from the solution for forming a solid amorphous ferroelectric material; and

10 stabilizing the ferroelectric material for minimizing changes in ferroelectric properties, the stabilizing being conducted at a temperature less than sufficient to crystallize the amorphous material.

2. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material
15 is selected from the group consisting of barium titanate, lithium niobate, strontium barium niobate, lead zirconium titanate, lead lanthanum zirconium titanate, yttrium oxide, zirconium oxide, tin oxide, titanium oxide, barium oxide and silicon oxide.

20 3. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material is a stoichiometric single metal oxide selected from the group consisting of the oxides of zirconium, tin,
25 titanium, yttrium, barium, silicon, vanadium, hafnium, tungsten, lanthanum and the lanthanide metals.

30 4. An amorphous ferroelectric material as recited in claim 1 wherein the amorphous ferroelectric material is a nonstoichiometric multiple metal oxide, and more specifically, a mixed metal oxide selected from the group consisting of $2[\text{Li}_x\text{Nb}_{(1-x)}\text{O}_y]$ where x is in the range of from 0 to 0.5 and $y = (5-4x)/2$, $\text{Pb}(\text{Zr}_x\text{Ti}_{(1-x)})\text{O}_3$ where x is in the range of from 0 to 1, and
35 $(\text{Sr}_x\text{Ba}_{(1-x)})\text{Nb}_2\text{O}_6$ where x is in the range of from 0.25 to 0.75.

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1 5. An amorphous ferroelectric material as recited
in any of the preceding claims wherein the amorphous
ferroelectric material is in the form of a film on a
substrate.

5 6. An amorphous ferroelectric material as recited
in any of the preceding claims wherein the substrate is
flexible.

10 7. An amorphous ferroelectric material as recited
in any of the preceding claims wherein the substrate
comprises an electrically conductive organic polymer.

15 8. A method for forming an amorphous
ferroelectric material as recited in any of the
preceding claims comprising the steps of:

preparing an anhydrous solution containing at
least one precursor compound for the material;

20 removing solvent from the anhydrous solution for
forming an amorphous solid material; and

heating the condensed amorphous material at a
sufficient temperature for stabilizing its polarization
properties and an insufficient temperature for
crystallizing the amorphous material.

25 9. A method as recited in claim 8 comprising the
step of depositing the solution as a film on a
substrate before completely solidifying the amorphous
material.

30 10. A method as recited in claim 8 wherein the
precursor compound comprises a metal alkoxide and
comprising the step of exposing the metal alkoxide to
water vapor for hydrolysis and polycondensation.

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- 1 11. A solid state electronic device comprising:
 a substrate;
 a circuit component on the substrate, a portion of
the circuit component comprising a film of amorphous
5 ferroelectric material as recited in any of the
preceding claims; and
 means for applying an electric field across at
least a portion of the film of amorphous ferroelectric
material.
- 10 12. A thin film of amorphous ferroelectric
material selected from the group consisting of barium
titanate, lithium niobate, strontium barium niobate,
lead zirconium titanate, lead lanthanum zirconium
15 titanate, yttrium oxide, zirconium oxide, tin oxide,
titanium oxide, barium oxide and silicon oxide.
13. An optical device including a transparent
film of amorphous ferroelectric material.
- 20 14. An optical device comprising:
 a crystalline ferroelectric substrate; and
 a thin film of amorphous ferroelectric material
deposited on the substrate.
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$\frac{1}{2}$

Fig. 1

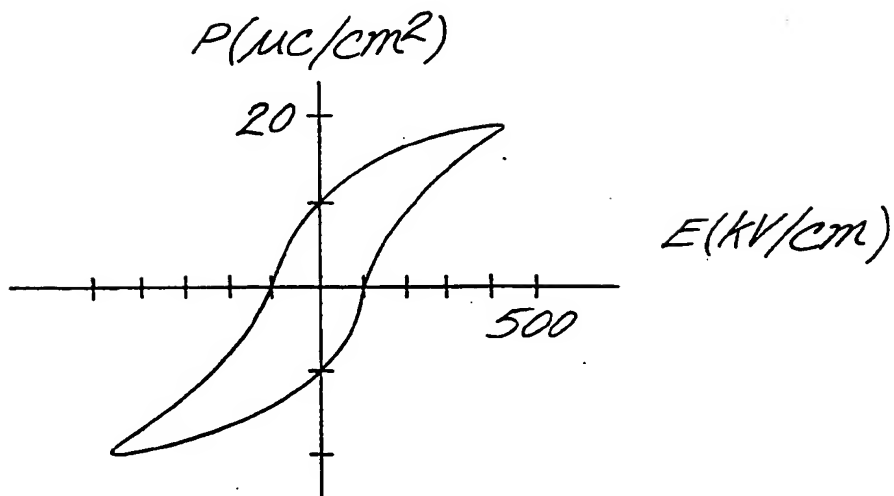
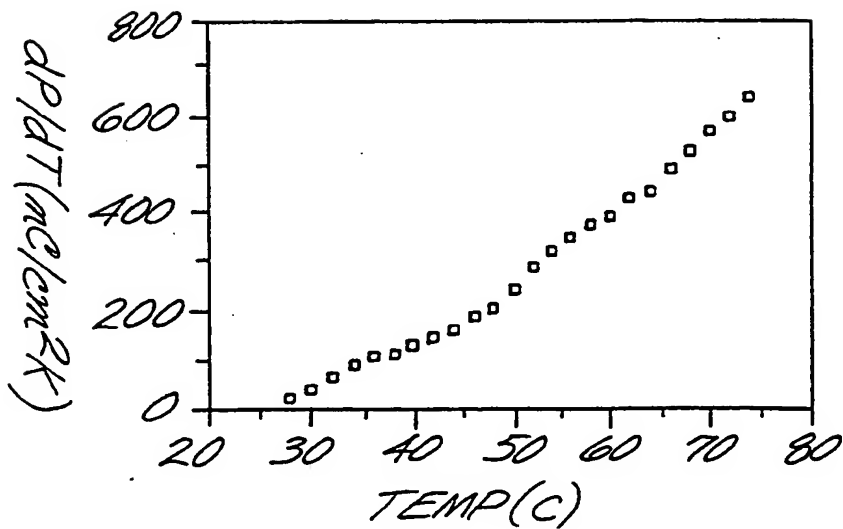


Fig. 2



2/2
Fig. 3

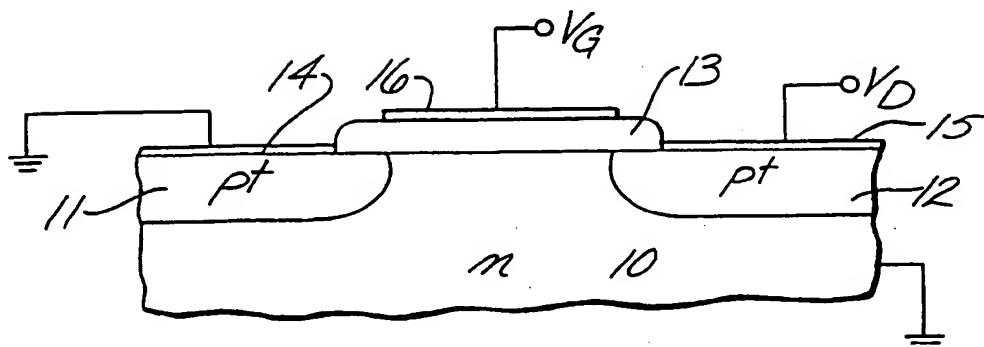


Fig. 4

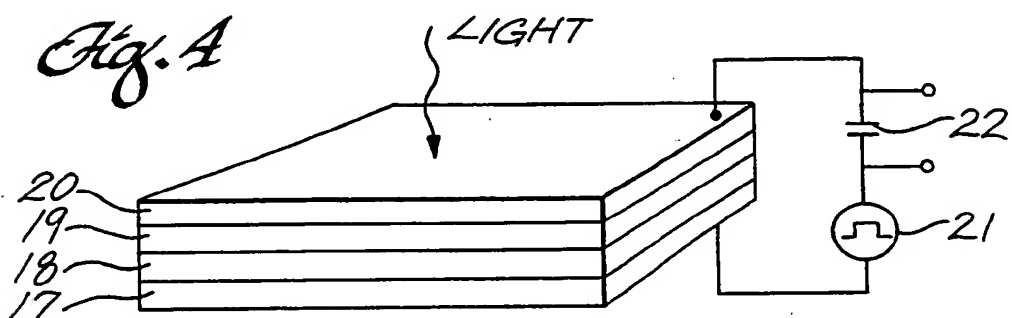
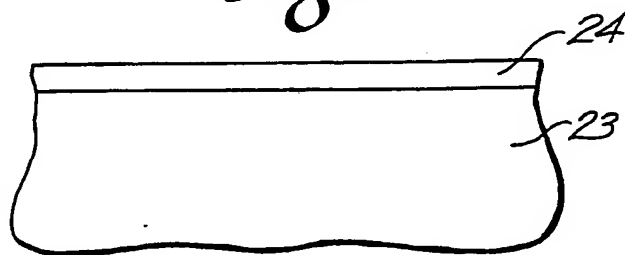


Fig. 5



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/03695**A. CLASSIFICATION OF SUBJECT MATTER**IPC(5) : C04B 35/46; B05D 5/12; B05D 3/12; B05D 3/02; C04B 35/49
US CL : 501/134,135,136,137,138; 427/100,126.3,346,376.2,385.5

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. :

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

Searched APS for inventors also terms "amorphous" or "glassy" or "non-crystalline" and "terraclectric" or "piezoelectric"

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	J. Appl. Phys., 1 September 1988, Yi et al., Preparation of Pb(Zr,Ti)O ₃ thin films by Sol gel processing: Electrical, optical, and electro-optic properties, p. 2717-2724. See entire document.	1-5,11-14
A	Mat. Res. Inc. Symp. Proc., 1986, Budd et al., The Effect of Hydrolysis Conditions on the Characteristics of PbTiO ₃ Gels and Thin Films, p. 317-322.	
A	Journal of Non-Crystalline Solids, 1988, Hirane, Formation of LiNbO ₃ Films by Hydrolysis of Metal Alkoxides, p. 538-541.	
A	Journal of Materials Science, 1984, Fukushima Preparation of Ferroelectric PZT Films by Thermal Decomposition of Organ-Metallic Compounds, p. 595-598.	
A	US, A, 3,660,155 (Mackenzie) 02 May 1972.	

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search

10 AUGUST 1992

Date of mailing of the international search report

24 SEP 1992

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